

ANILINE ELECTROCHEMICAL POLYMERIZATION AND CO-POLYMERIZATION WITH O-AMINOPHENOL ON BARE AND NAFION®-COATED STAINLESS STEEL: A POTENTIAL APPLICATION FOR CORROSION CONTROL

D. Sazou* and M. Kourouzidou

Department of Chemistry, Aristotle University of Thessaloniki,
54 124 Thessaloniki, GREECE

ABSTRACT

The aniline electrochemical polymerization and its co-polymerization with o-aminophenol on stainless steel (SS) and Nafion®-coated SS substrates is addressed in this paper. The cyclic potential sweep method (CPS) was used for the deposition of polyaniline (PAn) and copolymer films from monomer-containing 0.5 M H₂SO₄ solutions. Successive cyclic of the potential between -0.2 and 1.1 V results in copolymer films on both the bare SS and Nafion®-coated SS. The electrochemical response of copolymer films in monomerfree 0.5 M H₂SO₄ solutions exhibit different redox properties from those of PAn films. Scanning electron microscopy reveals also a more compact structure for the copolymer than the PAn film. The different redox behavior is due to the functional group -OH on the copolymer chain, which is associated with proton exchange resulting in an adjustment of the pH near the copolymer surface. Monitoring the open circuit potential of the copolymercoated SS electrodes versus time in comparison with that of PAn-coated electrodes indicates differences that may result in different corrosion protection properties. This is might be rationalized by considering different redox properties and thereby different structure of copolymer films.

Keywords: Polyaniline; o-aminophenol; copolymer; Nafion-polymer composite films; Corrosion control

INTRODUCTION

Polyaniline (PAn) is one of the most widely studied intrinsically electronic conducting polymers (IECPs) for metal and alloy corrosion control applications [1-6]. IECPs are considered as more environmentally friendly materials compared to chromate-based coatings. As with chromates, redox interactions of IECPs with metal and alloys are expected to occur resulting in a diminution of metal corrosion rates [7-21]. The electrochemical activity and good redox reversibility of PAn and its derivatives provide favorable conditions for their potential application as protective coatings ensuring a selfhealing effect [22-24]. Moreover, PAn is a stable in air polymer and can be easily synthesized by chemical and electrochemical methods [1].

Although PAn could impart anodic protection by maintaining the metal in the passive state, significant

advances are needed to improve the protective effectiveness of PAn coatings, for instance to increase the film adherence to the metal substrate, mechanical stability, long term protection ability mainly in chloride-containing solutions but also in less acidic (pH>4) solutions where the PAn degenerates. According to a possible basic mechanism considered as responsible for the corrosion protection and metal passivation induced by PAn, a necessary amount of H⁺ should surround the polymer film in order regeneration of the reduced form of PAn (emeraldine salt, ES) to take place [8,24]. The catalytic action of PAn involves Fe oxidation by ES, which is reduced to the leucoemeraldine (LE) whereas a further oxidation of ferrous to ferric ions and formation of the passive oxide along with the reoxidation of LE to ES occur by O₂.

* sazou@chem.auth.gr

Different strategies were implemented aiming to improve the protective effectiveness of PAN such as: (i) the introduction of dispersed platinum microparticles into the PAN film to ensure an enhanced O₂ reduction at dispersed platinum microparticles and replenishment of the PAN charge consumed by the stainless steel oxidation [25]; (ii) the use of PAN-epoxy or -acrylic blends that enhance mechanical properties of PAN coatings which contain proper doping anions (i.e. camphorsulfonate or phenylphosphonate) that form passivating complexes with iron cations providing an additional physical barrier to avoid penetration of chloride ions [26-28]; (iii) the pretreatment of the substrate with chelating agents [9] or other IECF films (i.e. polypyrrole) [29]; (iv) the use of large-size dopant anions (i.e. benzenesulfonate, salicylate, succinate) that cannot be readily exchanged during the doping process providing cationic permselectivity to the polymer and thus reducing the possibility of chloride insertion into the film [30].

Similar effect with that of the large-size dopant ions has the polymerization of An within a Nafion[®]-matrix [31]. The Nafion[®]-PAN composite films show a better protective behavior than the simple PAN films against pitting corrosion of stainless-steel (AISI 304) in chloride-containing acidic solutions due to the cation permselectivity of the Nafion[®] preventing Cl⁻ transport into the composite film [32]. In addition, sulfonate groups of the Nafion[®] contribute to the charge compensation of PAN and therefore charge transport processes involve proton expulsion than anion insertion.

Other strategies towards improving protection efficiency of PAN films involve composite polymers such as PAN with poly(o-toluidine) [33], but could also involve copolymers of the PAN. It was shown for example that the electrochemical copolymerization of An with o- or m-toluidine leads to the control of the copolymer conductivity in a broad range [34]. Other copolymers of PAN, for example with o-aminophenol (OAP) [35,36] and m-aminophenol [37] exhibit improved pH dependence of their electrical properties in comparison with the parent PAN. In general, successful copolymerization results in copolymers with PAN-like structure and

properties strongly affected by the monomers and their molar ratios [1].

The aim of this study is to synthesize poly(aniline-co-o-aminophenol) (P(An-co-OAP)) coatings on stainless steel (AISI 304) electrodes (SS) without and with Nafion[®] membranes with an ultimate goal the improvement of the anticorrosion properties of PAN coatings in chloride media. The copolymer, P(An-co-OAP), synthesized electrochemically in 0.5 M H₂SO₄ containing 0.1 M aniline and 5 mM o-aminophenol [35] by using cyclic voltammetry shows different electrochemical characteristics as compared with the PAN. The electrochemical activity of the copolymer is very good up to higher pH values (up to pH=9) and the redox behavior of the functional group -OH on the copolymer chain is associated with proton exchange resulting in an adjustment of pH near the copolymer surface [35,36]. Due to these properties, the copolymer is expected to have also improved anticorrosion properties.

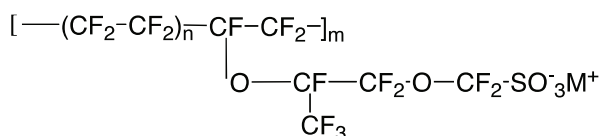
The composite Nafion[®]-copolymer was synthesized on the Nafion[®]-coated SS electrode by cyclic voltammetry in same solutions as for the bare SS. The Nafion[®] was predeposited at the surface of the SS electrode [31]. The electrochemical response of the prepared films shows that the redox properties of composite coatings were improved in comparison with those of simple polymers. Scanning electron microscopy was used to reveal the structure and morphology of polymer deposits. Monitoring the open circuit potential of the copolymer and composite films in Cl⁻-free and Cl⁻-containing sulfuric acid solutions was used as a first screening test to get evidence for their possible protective properties.

2. EXPERIMENTAL

Electrochemical measurements were performed by means of a VoltaLab 40 accompanied with the VoltaMaster 4 software from Radiometer Analytical. The working electrode was the cross section of a stainless steel (SS, AISI 304) wire 3 mm diameter (surface area = 0.0709 cm²) embedded in a 1 cm diameter PTFE cylinder. A volume of 100 ml was maintained in a three-electrode electrochemical cell. A Pt sheet (2.5 cm² in surface area) and a saturated calomel electrode (SCE) in a KCl solution were used

as counter and reference electrodes, respectively.

The poly(o-aminophenol) (POAP), PAn and P(An-co-OAP) films were deposited by sweeping the potential between -0.2 and 1.1 V from aqueous 0.5 M H₂SO₄ solution containing 5 mM o-aminophenol, 0.1 M aniline (An) (Fluka, puriss p.a.) and 0.1 M An + 5 mM OAP, respectively, prepared with H₂SO₄ (Merck, pro-analysis 96% w/w) using twice-distilled water. Nafion® films were prepared by placing a known volume (i.e. 89.6 µl) of Nafion® 117 (equivalent weight 1100) 5% w/v dissolved in a mixed solution of low aliphatic alcohols and water onto the SS by using a micro-syringe. The SS electrode was placed under a glass cover to shield the electrode from irregular air stream until a film was formed. The Nafion® films were dried for 24 hours at room temperature before use. The stock Nafion® 117 solution was purchased from Aldrich (Hydrogen Ion Form, Cat. No. 27,470-4). The structure of Nafion® used in this study is shown in Scheme 1, where M⁺ ≡ H⁺.



Scheme 1

To access the protective properties of polymeric films, chloride-containing solutions such as 0.5 M H₂SO₄+0.5 M NaCl were used in comparison with chloride-free 0.5 M H₂SO₄. The NaCl was purchased from Fluka and was puriss p.a. in purity. SS was purchased from Coodfellow Metals (Cambridge). The solution for electrochemical polymerization was deaerated with purified N₂ for 20 min before the beginning of each experiment. Measurements were carried out at room temperature, 22±2°C. Before each experiment the SS-disc electrode was polished by a series of wet sandings using different grit size (100, 180, 320, 500, 800, 1000, 1200 and superfine). After mechanical polishing, SS was rinsed first with twice-distilled water and after with ethanol under

ultrasonic agitation for 30 s in each solution.

Scanning electron microscopic observations were taken with a JEOL JSM-840A scanning electron microscope (SEM).

3. RESULTS AND DISCUSSION

3.1. Electrochemical synthesis of polymer films

3.1.1. On the SS electrode

The electrochemical polymerization of monomers was carried out on SS and Nafion®-coated SS electrodes by using the cyclic potential sweep (CPS) deposition. Deposition of polymer films was conducted by repeatedly sweeping the potential in the region between -0.2 and 1.1 V at dE/dt=20 mV s⁻¹. Figure 1 shows cyclic voltammograms (CVs) for the first 10 successive potential cycles, which indicate the formation of polymer films on the SS electrode. At the first cycle, the onset of the monomer oxidation appears at ~0.9 V due to the oxidation of the amino group in phenyl ring of the OAP and An. The gradual decrease of the current of this peak and increase of the current of anodic and cathodic peaks at lower potentials during cycling indicates the growth of films.

As can be seen in Figure 1a, in particular in the enlarged inset, a redox couple appears at 0.05 V due to the formation of the poly(ortho-aminophenol) (POAP). Apparently, the growth of POAP films proceeds at a very low rate as compared with that of polyaniline (PAn) films shown in Figure 1b. This is due to the low conductivity of the POAP, which inhibits the growth of the film [38,39]. During the reduction, a brown-orange material was seen to diffuse away from the SS surface towards the solution site indicating that a quantity of the oxidation product was removed away from the electrode resulting in a lower amount of deposits. However, after 20 potential cycles a thin dark blue-green film is seen on the SS surface.

On the contrary, the PAn film growth occurs at a

high rate as the rapid increase (in particular after the 4th cycle) of the current of anodic and cathodic peaks indicate in the range between 0.2 and 0.4 V as well as between 0.7 and 0.9 (Figure 1b). This is explained by an autocatalytic polymerization of the An in acidic solutions [40]. After 20 potential cycles a green film was formed on the SS surface.

The polymerization of An with OAP (An:OAP ratio equal to 20:1) takes place at intermediate rates (Figure 1c) as compared with those of the monomer alone (Figs. 1a,b). A first criterion for a successful copolymerization when using the CPS deposition is the closeness of the oxidation potentials of the two monomers. The onset of the OAP and An oxidation starts at very close potentials (Figs. 1a,b). A second criterion is the use of the appropriate molar ratio of the two monomers. In this study, the used An:OAP ratio was equal to 20:1 on the basis of copolymerization studies of OAP with An on a Pt electrode [35]. Figure 2c shows a similar behavior with that observed previously on Pt [35] indicating that copolymerization is also successful on SS where the film color is blue-green. As may be seen better in the enlarged CVs in Figure 1c there appear different anodic and cathodic peaks than those appear between -0.2 and 1.0 V during the polymerization of OAP (Figure 1a) and An (Figure 1b). Three anodic peaks at 0.2, 0.28 and 0.67 V (a broad one) with the corresponding cathodic peaks at 0.1, 0.22 and 0.38 V may be seen during the copolymerization. The broad anodic peak at ~0.67 V includes also the oxidation of the hydroxyl group in the phenyl ring of OAP. Comparing Figure 1b with Figure 1c shows an additional couple of oxidation and reduction peaks in Figure 1c at 0.28 and 0.22 V, respectively. In the case of the electrochemical copolymerization of An and OAP, the copolymer formation involves a head-to-tail coupling of two monomers as well as the polymerization of An [35,36]. Although the electrochemical response of the copolymer films shown in Figure 2 indicates the two main oxidation steps, as in the case of the PAn, there are differences in oxidation/reduction

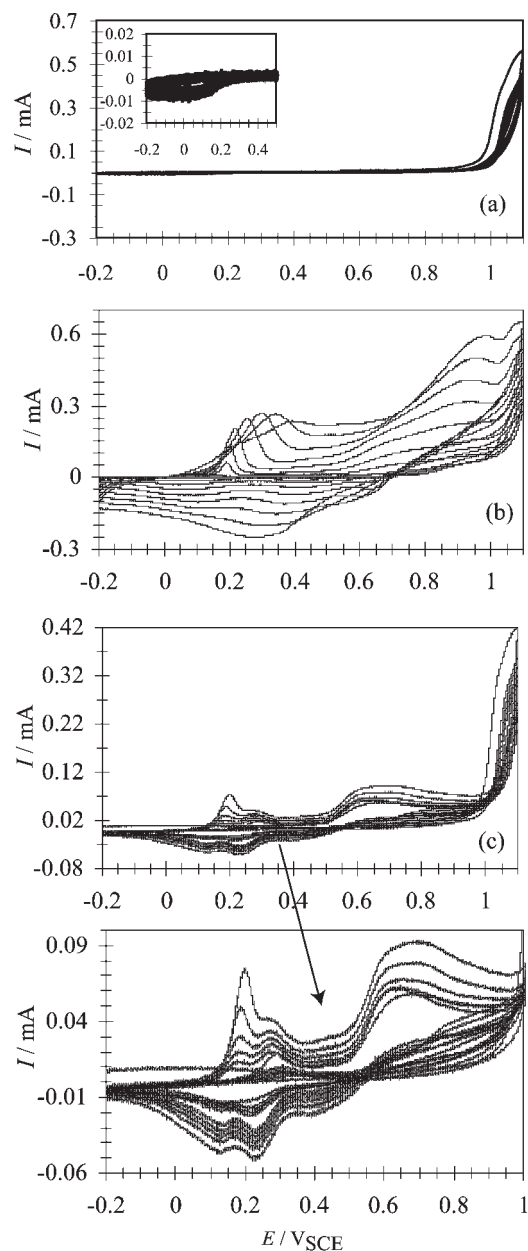


Figure 1 : Successive cyclic voltammograms for the first 10 cycles at $dE/dt=20 \text{ mV s}^{-1}$ during the growth of: (a) POAP, (b) PAn and (c) P(An-co-OAP) films on the SS electrode in aqueous solutions of $0.5 \text{ M H}_2\text{SO}_4$ containing 0.1 M An , 5 mM OAP and $0.1 \text{ M An}+5 \text{ mM OAP}$ (An:OAP ratio equal to 20:1), respectively. To get a more homogeneous deposition of PAn on bare SS a rotating SS-disc electrode at $\omega=250 \text{ r.p.m.}$ was used.

processes due to the different protonation extents and thus different doped ions of the nitrogen atoms in the copolymer chain due to the presence of the –OH group [36].

3.1.2. On the SS|Nafion® electrode

To obtain a copolymer film in which the insertion of pitting-induced anions, such as Cl⁻ ions, will be avoided, the electrochemical polymerization of An and OAP was carried out on a Nafion®-coated SS electrode. Nafion® is a cationic selective membrane, which is expected to be impermeable in anions [32]. Additionally, when the polymerization occurs within the Nafion® matrix, sulfonate groups act as counter ions resulting in a Nafion®-doped P(An-co-OAP) film. Similarly with self-doped PAn films [41,42], charge compensation processes are expected to involve only proton transport [43,44].

Figure 2 shows CVs obtained during the polymerization of OAP, An and An with OAP (An:OAP ratio equal to 20:1) on the SS|Nafion® electrode. CVs for the POAP synthesis (Figure 2a) show a lower rate of electropolymerization than on bare SS. This is attributed to an additional diminution of the film conductivity due to the presence of the Nafion® film. However, no material diffusion was observed during reduction as in the case of the bare SS indicating that polymerization occurs into the Nafion® matrix. A light brown film was obtained after 20 potential cycles in the range between -0.2 and 1.1 V.

Polymerization of An on the SS|Nafion® is much faster than that of the OAP as can be seen in Figure 2b. Although CVs of the PAn growth on the Nafion®-coated SS resemble those obtained on bare SS, there are two distinct differences: (i) the polymerization rate is lower as can be deduced from redox currents, and (ii) there is a significant shift of the anodic/cathodic peak potentials. Both differences indicate that polymerization on the SS|Nafion® electrode occurs within the Nafion® matrix implying conditions of a lower conductivity than on bare SS. The sulfonate groups attached to the Nafion® backbone play the role of counter anions and upon the oxidation the positively charged PAn is formed with the expulsion of H⁺ [45-47]. In fact, previous estimations of the stoichiometric ratio of

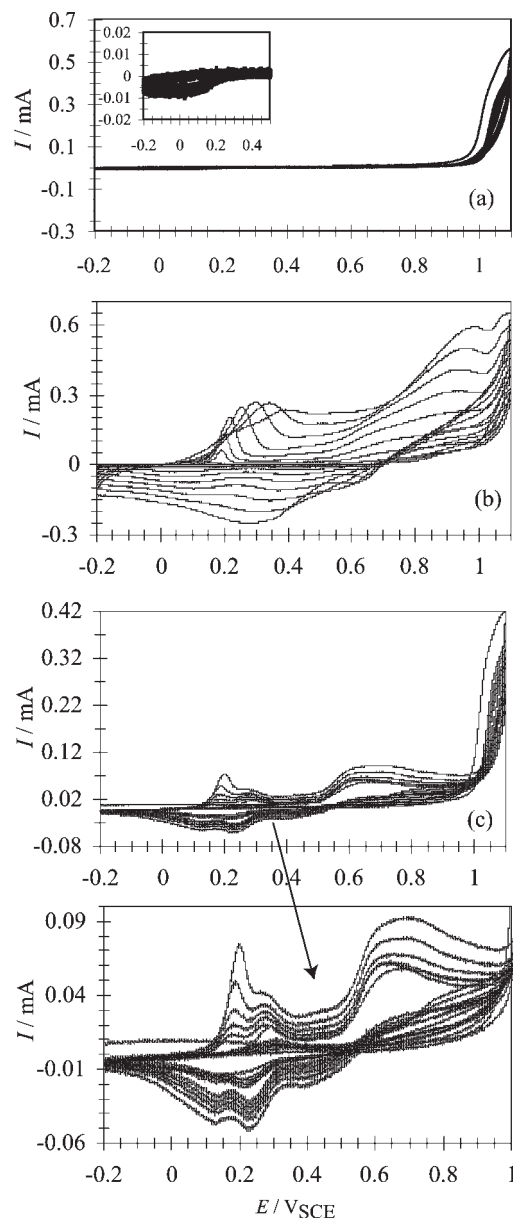


Figure 2 : Successive cyclic voltammograms for the first 10 cycles at $dE/dt=20 \text{ mV s}^{-1}$ during the growth of: (a) POAP, (b) PAn and (c) P(An-co-OAP) films on the SS|Nafion® electrode in aqueous solutions of 0.5 M H₂SO₄ containing 0.1 M An, 5 mM OAP and 0.1 M An+5 mM OAP (An:OAP ratio equal to 20:1), respectively. The significant shift of anodic/cathodic peaks observed during PAn growth is eliminated in the case of the copolymer growth.

sulfonate groups per aniline unit in the film showed that, by placing 89.6 μl of Nafion[®] on the SS under similar conditions used in this study for the An polymerization, sulfonate groups are in excess and can counterbalance the charge of PAn oxidized sites [31].

When electrochemical copolymerization occurs on the SS|Nafion[®] electrodes the CVs (Figure 2c) show essentially different redox activity from that observed during the growth of the POAP and PAn (Figs. 2a,b). The redox behavior is very good and CVs exhibit three anodic peaks at about 0.24, 0.48 and 0.65 V with the corresponding cathodic peaks at 0.15, 0.35 and 0.6 V. A dark blue film is obtained after 20 potential cycles indicating the formation of the composite Nafion[®]-copolymer film.

3.2. Electrochemical and SEM characterization of polymer films

The polymer-coated SS and SS|Nafion[®] electrodes prepared after 20 successive potential cycles were thoroughly rinsed with distilled water and transferred to the monomer-free polymerization solution. Curves 1 and 2 in Figure 3a are the CVs of PAn and P(An-co-OAP) films deposited on SS, respectively, in monomer-free 0.5 M H₂SO₄ 10 solution during the first potential sweep. CVs were traced at $dE/dt=10 \text{ mV s}^{-1}$ in the potential range between -0.2 and 0.95 V. It is clear that the redox behavior of copolymers differs from that of PAn. Curve 1 indicates the characteristic electrochemical response of the PAn film formed on SS by a CPS deposition in the range between -0.2 – 1.1 V. This response is in agreement with previous studies [23,31] and the polymerization curves shown in Figure 1b. It was shown previously [23] that upon increasing the upper potential limit from 0.8 to 1.1 V during CPS deposition there is a shifting of the PAn anodic/cathodic peak potentials that was attributed to hydrolysis products that lead to benzoquinone and/or quinoneimines [40,45]. Subsequent potential cycles causes even a greater shift of the anodic peaks to more positive potentials with a simultaneous degeneration [23,31]. Curve 2 in Figure 3a bears a great resemblance to that of P(An-co-OAP) on Pt [35]. It shows a sharp anodic peak at 0.28 V with a corresponding broader cathodic peak around 0.14 V. A second anodic process

appears as a current plateau between 0.4 and 0.7 V with a corresponding cathodic peak. It seems that the anodic current plateau as well as the cathodic peak, both consist of more than one peak. This behavior is in agreement with the polymerization curves (Figure 1c), where an additional couple of anodic/cathodic peaks appears. Subsequent cycles cause a lesser shift of anodic peaks to positive potentials and lesser degeneration of the copolymer in comparison with that observed for PAn films.

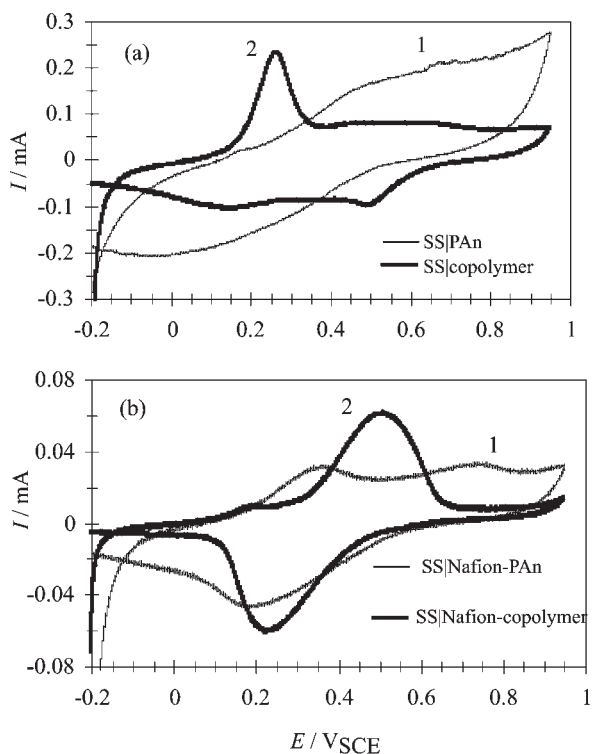


Figure 3 : Cyclic voltammograms of : (a) SS|PAn (curve 1) and SS|P(An-co-OAP) (curve 2) electrodes; (b) SS|Nafion[®]-PAn (curve 1) and SS|Nafion[®]-P(An-co-OAP) (curve 2) electrodes at $dE/dt=10 \text{ mV s}^{-1}$ between -0.2 and 0.95 V in a monomer-free 0.5 M H₂SO₄ solution. The films were formed after 20 potential cycles under the conditions used in Figs. 1 and 2.

The SS|Nafion[®]-PAn electrode shows two anodic peaks (two-stage oxidation of PAn) with the corresponding cathodic ones in the CV (first potential sweep) traced in the monomer-free 0.5 M H₂SO₄ (Figure 3b) at dE/dt=10 mV s⁻¹ between -0.2 and 0.95 V (curve 1 in Figure 3b). This behavior is in agreement with previous studies[31]. It was shown that subsequent potential cycles cause a gradual increase of the current of anodic/cathodic peaks, on the contrary to the simple PAn film [31]. There is no indication for the film degradation and a constant current is obtained after several potential cycles depending on the amount of PAn and Nafion[®] in the film. Similar behavior, without evidences for film degradation, is also observed for the Nafion[®]-copolymer film (curve 2 in Figure 3b). The Nafion[®]-P(An-co-OAP) film exhibits one anodic peak at ~-0.52

V with a shoulder at ~-0.18 V and one cathodic peak at ~-0.22 V.

The morphology and structure of films prepared by the CPS deposition on SS and SS| Nafion[®] electrodes was examined by scanning electron microscope (SEM). The SEM micrograph of Figure 4a shows a compact structure for the thin film of POAP formed on SS. On the contrary, the structure of the PAn film (Figure 4b) is characterized by few fibers and mostly by flakes or particles of a diameter in the range of 100-200 nm. The structure of the copolymer film shown in the SEM micrograph of Figure 4c bears resemblances to that of the PAn than that of the POAP film, but it appears to be essentially less porous than that of the PAn films.

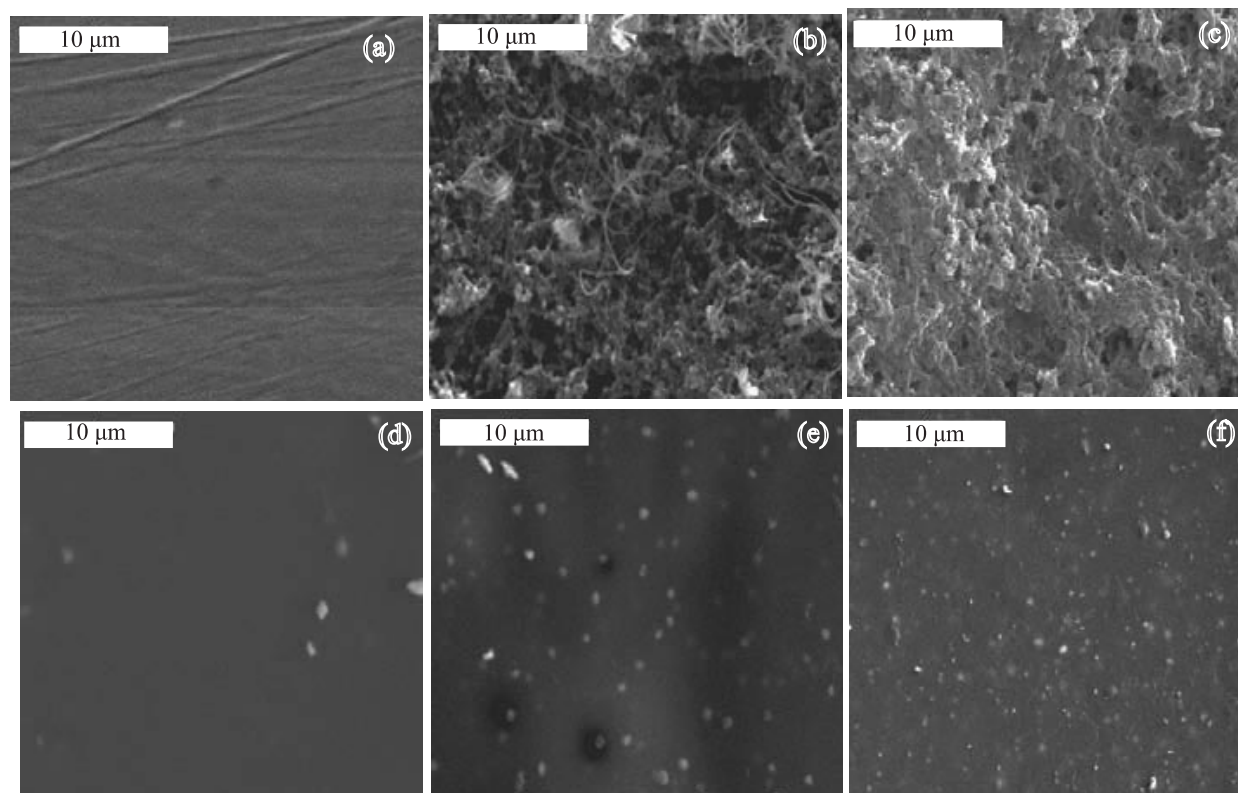


Figure 4 : SEM micrographs of simple films: (a) POAP, (b) PAn, (c) P(An-co-OAP), and composite films: (d) Nafion[®]-POAP, (e) Nafion[®]-PAn, (f) Nafion[®]-P(An-co-OAP) formed on SS and SS| Nafion[®] electrodes under the conditions used in Figures 1 and 2.

The SEM micrographs of the composite with Nafion® films shown in Figs. 4d-f do not show any particular morphology. This may indicate that polymers were homogenized well with Nafion® to provide a compact and smooth layer in nanosize dimensions that SEM fails to reveal. Light spots are distinguished for all composite films that are attributed to polymer or copolymer formed outside the Nafion® matrix. A lesser number of spots shown in Figure 4d for the Nafion®-POAP is due to the very low polymerization rate (Figure 2a). A larger number of spots seen in the case of the Nafion®-copolymer (Figure 4f) is in agreement with the higher polymerization rate and better electroactivity (Figure 2c) as compared with the composite Nafion®-PAN film (Figure 4e and Figure 2b).

3.3. Evidences for the protective ability of simple and composite copolymer films against corrosion of SS in acidic solutions without and with chlorides

The copolymer-coated SS and SS|Nafion® electrodes prepared by employing CPS deposition for 20 successive potential cycles were used for monitoring the open circuit potential (E_{OC}) versus time in a 0.5 M H_2SO_4 solution without and with Cl^- in comparison with the corresponding PAN-coated electrodes. The E_{OC} provides a measure for the protective properties of deposited films against corrosion of SS within a studied period of time. The E_{OC} for the bare SS and Nafion®-coated electrodes was also monitored versus time in the same corrosive media. It should be noted that the E_{OC} of the POAP-coated electrodes was measured and found to be very close to that of the POAP-free electrodes due rather to the low amount of polymer deposited by CPS.

The E_{OC} of the bare SS is stabilized in the active state at approximately -0.45 ± 0.02 V in a 0.5 M H_2SO_4 solution, without and with Cl^- . It remains nearly at this range after several days of immersion. On the contrary, as Figure 5a shows, the E_{OC} of the PAN-

and P(An-co-OAP)-coated SS electrodes in a 0.5 M H_2SO_4 solution shifts to very positive potentials (>0.4 V) with respect to the E_{OC} of the bare SS. This indicates that both film-coated SS electrodes remain in the passive state. The E_{OC} of the copolymer-coated SS is approximately 0.07 V less positive than that of the PAN-coated SS electrode. This might be due either to the different redox behavior, which is shifted to lesser positive potentials (Figure 3a) or to the lesser conductivity of the copolymer in comparison with the PAN film [35].

The E_{OC} of the SS|PAN electrode is higher than that of the SS|P(An-co-OAP) one also in the presence of Cl^- , but only during the first 10 min of the measurement (Figure 5b). The E_{OC} of the

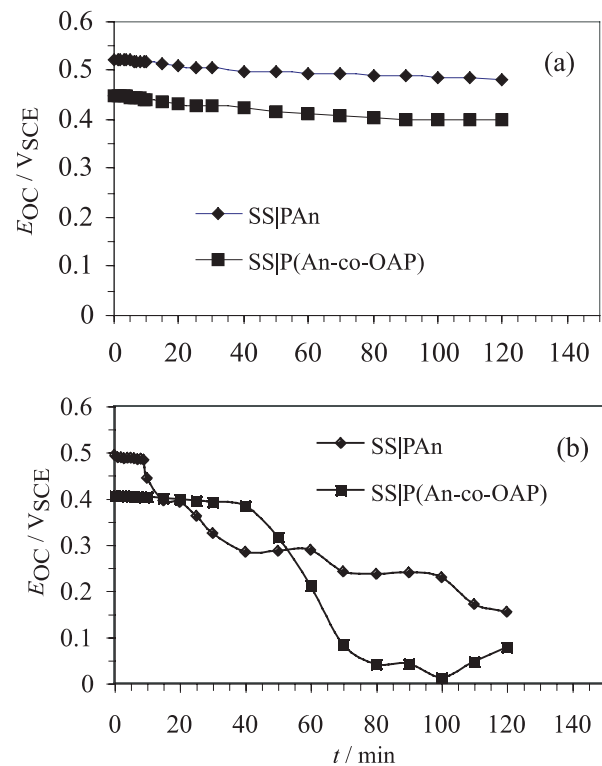


Figure 5 : Open circuit potential (E_{OC}) as a function of time for SS|PAN and SS|P(An-co-OAP) electrodes in (a) 0.5 M H_2SO_4 and (b) 0.5 M H_2SO_4 + 0.5 M NaCl.

SS|P(An-co-OAP) electrode remains constant at ~ 0.4 V for a longer time (~ 1 h) than that of the SS|PAn electrode. At even a longer time, the E_{OC} of the former electrode shifts to lower values, although there is a tendency of convergence between the E_{OC} of the two electrodes. Nevertheless, although the E_{OC} of both electrodes is much lower after ~ 2 h of immersion in Cl^- -containing solutions than that in Cl^- -free solutions, it still remains in the passive state. It should be noticed, however, that the lowering of the E_{OC} is due to the Cl^- -induced localized corrosion [48] since visual observations reveal pits on the SS surface underneath the films. Pitting corrosion may be induced by Cl^- that may transport through the polymer film to reach the SS substrate since the positively charged PAn and copolymer films in their partially oxidized states both may attract solution anions, including Cl^- , during doping [49].

The fact that the E_{OC} of the SS|PAn electrode drops faster to lower values as compared with that of the SS|P(An-co-OAP) electrode may be rationalized by considering the chemical composition and structure of the films resulting in different redox behavior. As Figure 3 shows the electrochemical response of the copolymer indicates a better redox behavior than that of PAn. Higher rates of corrosion in Cl^- -containing solutions demand a more rapid oxidizing ability from the coating to repair the passive film at rates of the same order with those by which it is broken down by Cl^- . The lesser ability of the PAn film in comparison with the copolymer film may be due to the decrease of the partially oxidized units of the polymer or to the higher degree of degradation observed for the PAn (Figure 3). Moreover, according to the SEM observations, the structure of the copolymer appears to be more compact than that of the PAn (Figure 4).

Using either a membrane that does not allow transport of anions or self-doped polymers that do not exchange anions with solution might render chloride insertion into the polymer during doping and avoid pitting of the substrate. Both effects are expected to occur when using Nafion®-coated SS electrodes. Figure 6 shows the E_{OC} of both the SS|Nafion®-PAn and SS|Nafion®-P(An-co-OAP) measured in $0.5 \text{ M H}_2\text{SO}_4$ solutions without and with Cl^- . In Cl^- -free solutions (Figure 6a), the E_{OC} of both electrodes (Figure 5a), 14 remains stable in the passive state at sufficiently positive potentials (~ 0.45 V for the PAn and ~ 0.3 V for the copolymer) even after several hours (~ 10 h) of monitoring.

A great difference between the E_{OC} of the SS|PAn and SS|P(An-co-OAP) SS and that of the corresponding SS|Nafion® electrodes appears in the Cl^- -containing solutions. Comparing Figure 6b with Figure 5b shows that the EOC of both the SS|Nafion®-PAn and SS|Nafion®-P(An-co-OAP) electrodes does not drop to low values as in the case of the corresponding SS electrodes. The E_{OC} for the Nafion®-copolymer film remains at the same value with that measured in the absence of Cl^- (Figure 6a), whereas the E_{OC} for the Nafion- PAn is lower by ~ 0.05 V in the presence of Cl^- . It is notable, however, that during the studied time the E_{OC} of both composite films remains stable in the presence of Cl^- . This behavior suggests that Nafion® prevents the transport of Cl^- through the film and pitting corrosion is avoided [31]. The E_{OC} of the polymer-free SS|Nafion® electrodes with and without chlorides is higher (~ 0.2 V) compared with that of the SS bare electrode, but is lower than that of the PAn- and copolymer-composite ones. Thus the composite with Nafion® films seem to provide an effective inhibition of the pitting corrosion of SS in Cl^- -containing sulfuric acid solutions.

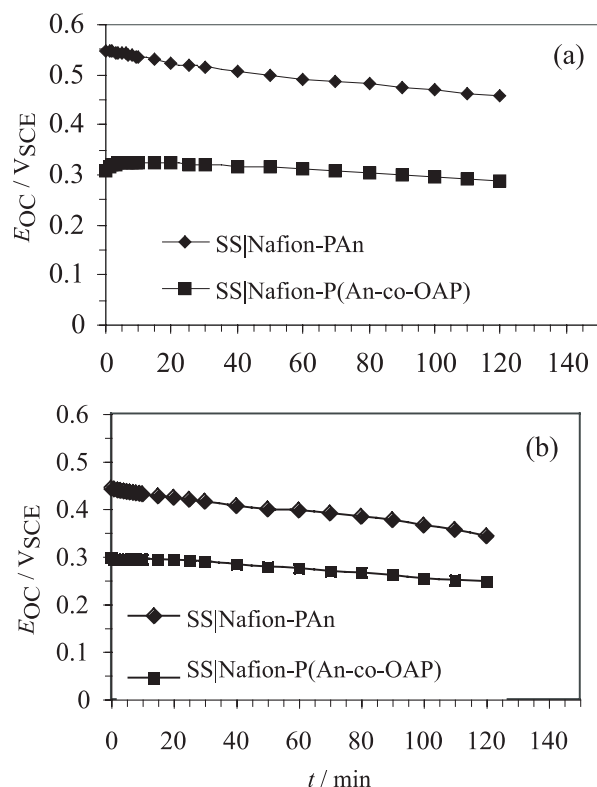


Figure 6 : Open circuit potential (E_{oc}) as a function of time for SS|Nafion[®]-PAN and SS|Nafion[®]-P(An-co-OAP) electrodes in (a) 0.5 M H₂SO₄ and (b) 0.5 M H₂SO₄ + 0.5 M NaCl.

In addition, the potentiodynamic I - E curves of the SS|Nafion[®]-PAN and SS|Nafion[®]-P(An-co-OAP) electrodes in 0.5 M H₂SO₄+0.5 M NaCl solutions show the redox behavior of the composite films, similarly with that in the Cl⁻-free 0.5 M H₂SO₄ solutions, indicative of a complete inhibition of the Cl⁻ transport into the film. Similar behavior seems to appear also in neutral Cl⁻-containing solutions where preliminary experiments were carried out. On the contrary, I - E curves of the SS|PAN and SS|P(An-co-OAP) electrodes show high dissolution currents due to pitting corrosion induced by Cl⁻. Further experiments are in progress to evaluate further the long-term protective efficiency of simple and composite copolymer films.

4. CONCLUSIONS

The electrochemical copolymerization of aniline with o-aminophenol on SS results in copolymer films that exhibit different redox behavior and they are more compact in structure compared with the PAN films. The copolymerization rate is inhibited by the presence of o-aminophenol but is much faster than that of the POAP growth. The oxidation/reduction processes of the copolymer appear at less positive potentials than those of PAN due the functional group -OH on the copolymer chain, which is associated with proton exchange resulting in an adjustment of pH near the copolymer surface.

The preliminary study shows that copolymer films might provide protection against pitting corrosion for a longer time than PAN films but most importantly, Nafion[®]-copolymer films should almost completely prevent chloride transport and thus pitting corrosion to occur. The redox activity of the Nafion[®]-copolymer film differs from that of the Nafion[®]-PAN film and further studies are necessary to clarify polymerization processes into the Nafion[®] matrix. The mechanism by which the composite with Nafion[®] films provides protection in chloride-containing solutions might be understood by considering: (i) the cationic permselectivity of Nafion[®] that prevents chlorides to transport into the composite layer, and (ii) the contribution of proton transport than anions in charge compensation processes due to the fact that sulfonate groups of the Nafion[®] function as inner dopants.

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